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(71) Applicant
Corning Glass Works,
Corning, New York 14830,
United States of America.
(72) Inventor
Ralph Allan Messing
(74) Agents
Elkington & Fife

(54) **Hydrophobic inorganic membrane for gas transport**

(57) A controlled-pore inorganic membrane wherein at least 90 percent of the pores have diameters of from 10 to 10,000Å is rendered hydrophobic so as to permit the transport of one or more gases from or into an aqueous medium while preventing the passage of water therethrough, and to allow the separation of hydrophobic gases from a mixture of hydrophobic and hydrophilic gases.

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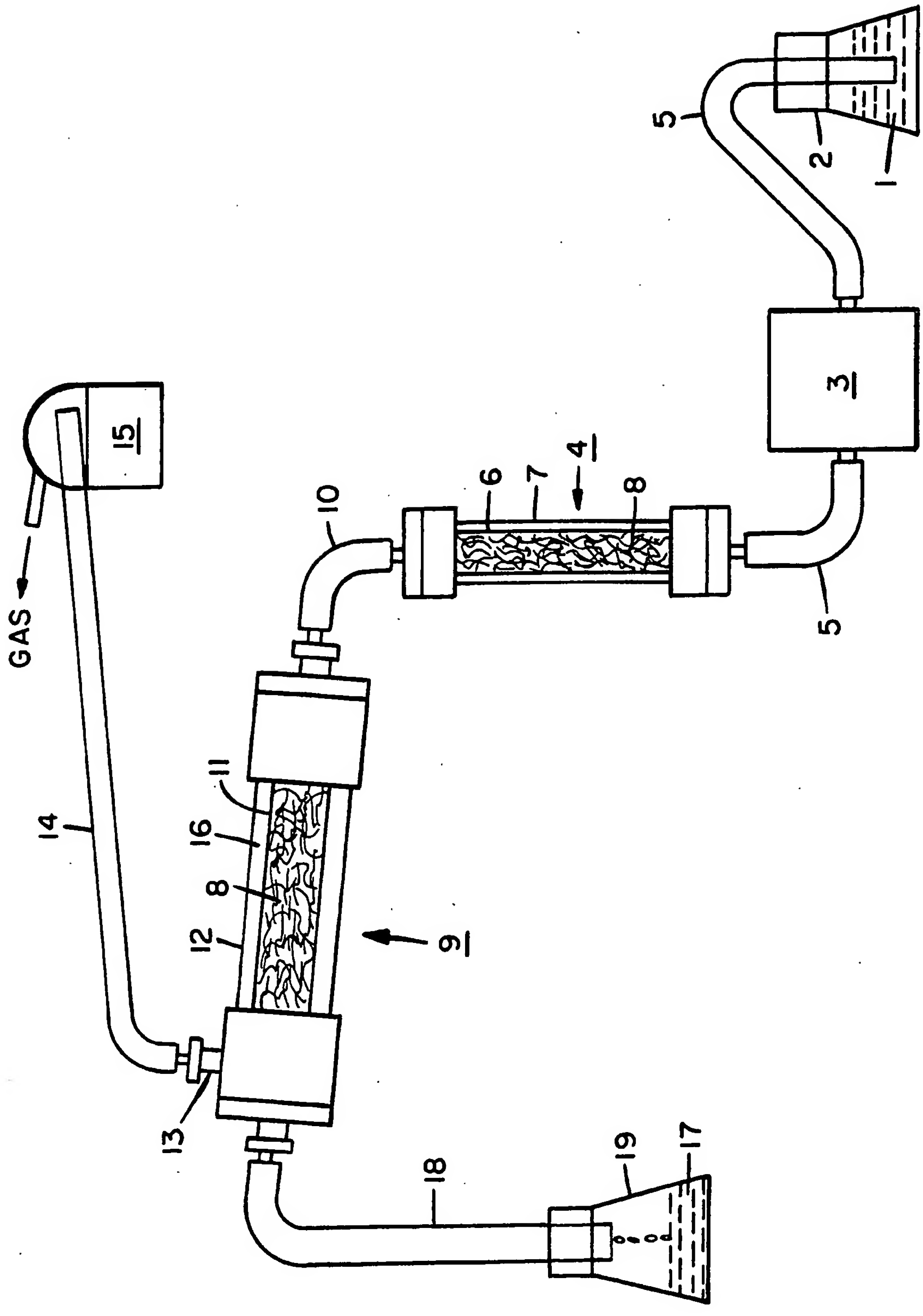
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SPECIFICATION

## Controlled-pore, Hydrophobic Inorganic membrane for Gas Transport

This invention relates to a controlled-pore, hydrophobic inorganic membrane for gas transport; more particularly, it relates to a controlled-pore, hydrophobic inorganic membrane in which at least 90 percent of the pores have diameters of from 100 to 10,000Å.

In general terms, the present invention relates to a means for achieving gas transport from or into an aqueous medium, and to a controlled-pore, hydrophobic inorganic membrane which permits the transport of one or more gases from or into an aqueous medium while preventing the passage of water therethrough.

Various industrial and laboratory processes require the introduction of one or more gases into an aqueous reaction medium. Examples of such gases include, for example, air or oxygen, carbon dioxide, hydrogen sulphide, sulphur dioxide, hydrogen and chlorine. Typically, such gases are introduced into the aqueous medium from a point source which, if desired, may be fitted with a fritted glass sparger to increase the gas-liquid interface. Nevertheless, vigorous agitation is required to distribute the gas throughout the liquid, thereby enhancing dissolution or reaction. Unless the gas is extremely soluble in or reaction with the aqueous medium, a considerably excess of gas must be employed. Furthermore, at the conclusion of gas introduction, the liquid medium may, and usually does, back up into the gas introduction tube, especially when the gas is highly reactive or soluble.

Other industrial and laboratory processes evolve gases which must be handled in some way, for example collected, measured or employed as a reactant. In such cases, there often is little which may be done to expedite gas removal. For example, it is well known that the solubilities of many gases in water are inversely proportional to the temperature of the aqueous medium. Increasing the temperature of the aqueous medium to decrease gas solubility may not be feasible, however, if increased reaction rates cannot be controlled or are not desirable, or in those cases where one or more reactants or products are heat-sensitive. While reducing the pressure above the aqueous medium may often aid the removal of gases dissolved therein, such a procedure is frequently not practical. The reduction of pressure will obviously increase the rate of conversion of liquid water to water vapour, an often undesirable result. In addition, the premature or unwanted removal of a reactant or reaction product may occur in those cases where the vapour pressure of such reactant or reaction product is significantly higher than that of water. Furthermore, equipment requirements may become quite complex, especially when substantial pressure reductions are required.

In accordance with the present invention, there is provided a controlled-pore, h[illegible] [illegible] have diameters of from 100 to 10,000Å. Such a membrane permits the transport of one or more gases from or into an aqueous medium while preventing the passage of water therethrough. Such transport is uniform over the entire surface area of the membrane and, in the case of transporting a gas into the aqueous medium, achieves a high gas-liquid interface without the need for agitation means or excessive gas consumption.

Also in accordance with the present invention, there is provided a process for preferentially extracting one or more hydrophobic gases from a mixture of hydrophobic and hydrophobic gases which comprises:(a) presenting such mixture of hydrophobic and hydrophilic gases to one side of a controlled-pore, hydrophobic inorganic membrane in which at least 90 percent of the pores have diameters of from 100 to 10,000Å; and

(b) withdrawing from the other side of the membrane a hydrophobic gas-enriched mixture of gases.

Referring to the accompanying drawing, the drawing illustrates one embodiment of the present invention as described in Examples 1 and 2, which embodiment comprises treating sewage to give an effluent having a significantly reduced oxygen demand and methane as a gaseous product. As used herein, the term "membrane" refers to a continuous, formed article, the shape and dimensions of which are adapted to the apparatus to be employed and process requirements. Thus, the membrane may be a flat or curved sheet, a three-dimensional article, such as a rectangular or cylindrical tube, or a complex monolith having alternating channels for gas and aqueous medium. As a practical matter, the membrane most often will consist of a cylinder, open at both ends to provide passage of aqueous medium through its length. Wall thickness is not critical, but must be sufficient to permit the membrane to withstand process conditions without deformation or breakage. In general, a wall thickness of at least 1.0 mm is desired.

The membrane may be either siliceous or non-siliceous metal oxides. Examples of siliceous materials include, for example, glass, silica, wollastonite and bentonite. Examples of non-siliceous metal oxides include, for example, alumina, spinel, apatite, nickel oxide and titania. Siliceous materials are preferred, with glass and silica being most preferred. Of the non-siliceous metal oxides, alumina is preferred.

The membrane must have a controlled porosity such that at least 90 percent of the pores have diameters of from 100 to 10,000Å. Preferably, the pore diameter range will be from 900 to 9,000Å, most preferably from 1,500 to 6,000Å.

Methods of preparing inorganic membranes having controlled porosity as described above are well known to those skilled in the art and, for further details, reference may be made, for example, to U.S. Patent Nos. 2,106,764; 3,485,687; 3,549,524; 3,678,144; 3,782,982; 3,827,893; 3,850,849 and 4,001,144; British Patent No. 1,392,220; and Canadian Patent No. 952,289. In addition, various [illegible]c materials are commercially avail-

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able which may be formed into shaped articles by known methods. Among suppliers of such porous inorganic materials are the following: Alcoa; Catalytic Chemical Co. Ltd.; Coors; Corning Glass Works; Davison Chemical; Fuji Davison Co. Ltd.; Harrisons & Crosfield (Pacific) Inc.; Kaiser Chemicals; Mizusawa Kagaku Co. Ltd.; Reynolds Metals Company (Chemicals Division); Rhodia, Inc. (Chemical Division); and Shokubai Kasei Co. Ltd.

As a second requirement, in addition to controlled porosity, the present inorganic membrane must be hydrophobic. Since the inorganic materials of which the membrane is usually composed are not inherently hydrophobic, the property of hydrophobicity must normally be imparted to the membrane by treating it either before or after the membrane is shaped or formed. As a practical matter, such treatment will usually be a post-formation treatmeent. The nature of the treatment is not critical and various treatments which will render the membrane hydrophobic may be employed. The property of hydrophobicity, however, must be imparted throughout the entire void volume of the membrane and not just to the external surface areas.

Hydrophobicity is most conveniently imparted to the shaped or formed membrane by immersing the membrane in an organic solvent which contains dissolved therein a suitable hydrophobic reagent, removing the membrane from the solvent and allowing it to air dry. Although the concentration of the reagent is not critical, an especially useful concentration range has been found to be from 3 to 25 percent, weight per volume of solvent. A most convenient concentration is about 10 percent. Various solvents in which the hydrophobic reagent is soluble may be employed. Examples of suitable solvents include: hexane, cyclohexane, diethyl ether, acetone, methyl ethyl ketone, benzene, toluene, the xylenes, nitrobenzene, chlorobenzene, bromobenzene, chloroform and carbon tetrachloride. Examples of suitable hydrophobic reagents include: natural waxes, such as spermaceti, beeswax, Chinese wax and carnauba wax; synthetic waxes, such as cetyl palmitate, cerotic acid, myricyl palmitate and ceryl cerotate; aliphatic hydrocarbons, such as octadecane, eicosane, docosane, tetracosane, hexacosane, octacosane, triacontane and pentatriacontane; polycyclic aromatic hydrocarbons, such as naphthalene, anthracene, phenanthrene, chrysene and pyrene; polybasic acids, such as Empol Dimer Acid and Empol Trimer Acid (Emery Industries, Inc.); polyamide resins, such as the Emerez Polaymide Resins (Emery Industries, Inc.); water-insoluble polymeric isocyanates, such as poly(methylenephenylisocyanate) which is commercially available as PAPI (Upjohn Company); and alkylhalosilanes, such as octadecyltrichlorosilane and di(dodecyl)difluorosilane. The alkylhalosilanes are preferred, with octadecyl-trichlorosilane being most preferred.

From the foregoing, it should be apparent to those skilled in the art that various hydrophobic reagents which will adhere to the inorganic membrane with a reasonable degree of permanence may be employed. Such adher purely physical means, such as van der Waals attraction, by chemical means, such as ionic or covalent bonding, or by a combination of physical and chemical means.

One of the characteristics of the present membrane is a preference for hydrophobic gases. Thus, when a mixture of hydrophobic and hydrophilic gases is presented to one side of the membrane, the hydrophobic gas or gases will pass through in preference to the hydrophilic gas or gases. Accordingly, this characteristic makes it possible preferentially to extract one or more hydrophobic gases from a mixture of hydrophobic and hydrophilic gases.

The present controlled-pore, hydrophobic inorganic membrane may be employed in accordance with known procedures, and the adaptation of the present membrane to known processes will be apparent to those skilled in the art. For example, in a batch process, a reaction vessel may be divided into two compartments by means of the present membrane. The membrane may be horizontal or vertical or at a desired angle, with one compartment being charged with an aqueous reaction medium. If it is desired to introduce a gas into the aqueous medium, the other compartment is charged with such gas, usually under slight pressure (e.g. less than 1Kg/sq.cm (15 psig)). If a gaseous reaction product is to be removed, such other compartment may be vented to the atmosphere or maintained under slightly reduced pressure.

It should be apparent to those skilled in the art that the present membrane is best suited for use in continuous processes. Under such circumstances, the membrane will normally be shaped in such a manner as to provide one or more channels for the passage of a fluid, e.g. a cylinder which is open at both ends. Thus, the aqueous medium may flow through such channels or around the exterior of the membrane. Furthermore, the gas to be introduced or removed may be dissolved in a liquid solvent having a high affinity for the gas, i.e. in which the gas has a high degree of solubility. Suitable solvents for many gases include silicones and fluorocarbons. In a typical embodiment, the aqueous reaction medium is circulated through the channel enclosed by, for example, a cylindrical membrane. The membrane in turn is enclosed within a second, larger cylinder which is impervious to both gases and liquids. Such second cylinder will most commonly be made of glass. Gas is introduced into or removed from the enclosed area between the membrane and the second cylinder.

The present invention is further described with reference to the accompanying drawing, by the following Examples which illustrate the use of the present membrane in the treatment of sewage.

Sewage 1 is pumped from container 2 by pump 3 to aerobic reactor 4 via rubber tubing 5 sealably connected to the pump and the aerobic reactor. The aerobic reactor consists of inner glass tube 6 sealably enclosed within glass jacket 7. The inner glass tube contains an inorganic carrier 8 such as that described in U.K. Patent No. (application No. 4333,278) which is suitable for the

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accumulation of a biomass. Sewage leaving the aerobic reactor is transported to anaerobic reactor 9 via rubber tubing 10 sealably connected to both reactors. The anaerobic reactor consists of the present inorganic membrane 11 and glass jacket 12 having exit port 13. The inorganic membrane is filled with additional inorganic carrier 8 and is sealably enclosed within the glass jacket. Rubber tubing 14, sealably connected to the exit port of the jacket, leads to pump 15 which removes gas (methane) from air space 16 enclosed by the jacket. Such gas is in turn collected by a suitable means, such as by the displacement of water in an inverted vessel (not shown). Sewage effluent 17 then is transported, via rubber tubing 18 sealably connected to the anaerobic reactor, to receiving vessel 19.

The sewage employed in each of the examples was obtained from the inlet pipe to the Corning, New York, U.S.A. Municipal Sewage Waste Treatment Plant. The sewage was stored at from 4 to 6°C. Prior to use, the sewage was filtered through cheesecloth and glass wool to remove coarse particulate matter. Sewage was collected either weekly or biweekly.

*Example 1*

Pump 3 consisted of a Fluid Metering pump, RP1G6CSC (Fluid Metering, Inc., Oyster Bay, N.Y. U.S.A.), which was connected to aerobic reactor 4 using a 35 cm. (14") length of rubber tubing. A 50 cm. (20") length of rubber tubing was attached to the intake side of the pump and led from a flask containing sewage.

The aerobic reactor consisted of a Pharmacia K 16/20 column (Pharmacia Fine Chemicals, Uppsala, Sweden) with water jacket; the water jacket was left vented to the atmosphere. The column was charged with 24 g. of cordierite (CGZ) carrier having a pore diameter distribution of from 2 to 9 μ and an average port diameter of 4.5 μ. The carrier was seeded with sewage microbes obtained previously.

The inorganic membrane 11 of anaerobic reactor 9 was a silica membrane, prepared in accordance with known procedures see, for example, U.S. Patent Nos. 3,678,144; 3,782,982 and 3,827,893. The membrane was approximately 18 cm. long with the following cross-sectional dimensions: 10.5 mm. i.d. and 15.5 mm. o.d. The average pore diameter of the membrane was 3500Å with a pore diameter distribution of from 2000 to 3600Å. Wall porosity was 60 percent and pore volume was 0.89 cc/g. The membrane was rendered hydrophobic by placing it in 75 ml. of a 10 percent solution of octadecyltrichlorosilane in acetone and allowing it to soak overnight. The membrane then was removed from the solution, washed with 500 ml. of acetone and air-dried.

The membrane was mounted in a Pharmacia K16/20 water jacket by means of the standard rubber sealing ring and threaded locking ring and was charged with 10 g. of the CGZ carrier. Both reactors together had a total void or fl[illegible]

The two reactors were coupled using about 10 cm (4") of rubber tubing. One of the ports of the anaerobic reactor jacket was sealed by attaching a short piece of "Tygon" tubing thereto and closing the tubing by means of a clamp. The other port was attached to a Buchler Polystaltic Pump (Buchler Instruments, Inc., Fort Lee, N.J. U.S.A.) using a length of thick-walled "Tygon" tubing. Gas evolved and passed through the membrane was collected by the displacement of water in a calibrated cylinder inverted in a water-filled, large, shallow vessel. The rate of gas evolution was observed and the collected gas was analyzed at least daily by mass spectrometry. In addition, the chemical oxygen demand (COD) of the sewage used as feed and the effluent emerging from the anaerobic reactor were determined periodically by conventional, well-known colourimetric dichromate oxidation procedures.

The process was run for a period of about nine months. Although data were generated on a daily basis, except for COD analyses, weekly averages of the data are presented in Table I below; in the Table, COD analyses are averaged where more than one analysis was obtained per week.

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*Table 1*
*Summary of Data Obtained in Example 1*

| *Week* | *Feed Rate, ml/hr.* | *Gas Evolved ml/hr.* | *Gas Composition (mole-%)* | | | | |
|---|---|---|---|---|---|---|---|
| | | | $CH_4$ | $CO_2$ | $O_2$ | $N_2$ | *A* |
| 1 | 10.4 | 16.0 | 1.1 | 3.8 | 11.8 | 82.2 | 1.1 |
| 2 | 10.8 | 4.6 | 9.3 | 6.8 | 11.4 | 71.4 | 1.1 |
| 3 | 10.8 | 2.5 | 17.8 | 1.4 | 8.6 | 71.3 | 1.0 |
| 4 | 10.0 | 0.9 | 44.0 | 2.6 | 5.1 | 47.4 | 0.9 |
| 5 | 8.5 | 1.7 | 59.8 | 4.9 | 3.5 | 31.2 | 0.6 |
| 6 | 22.0 | 1.9 | 57.0 | 4.3 | 3.9 | 34.0 | 0.7 |
| 7 | 23.0 | 1.4 | 36.8 | 3.6 | 4.8 | 53.8 | 1.0 |
| 8 | 23.0 | 2.2 | 56.4 | 3.4 | 3.6 | 35.9 | 0.7 |
| 9 | 22.7 | 1.2 | 39.0 | 2.8 | 4.6 | 52.6 | 1.0 |
| 10 | 23.0 | 1.6 | 47.1 | 3.1 | 3.6 | 45.4 | 0.9 |
| 11 | 22.3 | 0.4 | 20.3 | 2.2 | 10.9 | 65.1 | 1.3 |
| 12 | 22.4 | 0.6 | 23.7 | 3.1 | 37.5 | 64.3 | 1.3 |

*Table 1* (contd.)
*Summary of Data Obtained in Example 1*

| *Week* | *COD* | | | |
|---|---|---|---|---|
| | *In* | *Out* | *% Reduction* | *Remarks* |
| 1 | - | - | - | |
| 2 | - | - | - | a |
| 3 | - | - | - | b |
| 4 | - | - | - | |
| 5 | - | - | - | c |
| 6 | - | - | - | d |
| 7 | - | - | - | |
| 8 | - | - | - | |
| 9 | - | - | - | |
| 10 | - | - | - | e |
| 11 | - | - | - | f |
| 12 | - | - | - | g |

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*Table 1* (Continued)
*Summary of Data Obtained in Example 1*

| *Week* | *Feed Rate, ml/hr.* | *Gas Evolved, ml/hr.* | *Gas Composition (mole-%)* | | | | |
|---|---|---|---|---|---|---|---|
| | | | $CH_4$ | $CO_2$ | $O_2$ | $N_2$ | *A* |
| 13 | 22.7 | 0.6 | 37.2 | 3.1 | 5.9 | 52.7 | 1.2 |
| 14 | 21.5 | 1.6 | 65.2 | 6.0 | 3.2 | 24.9 | 0.6 |
| 15 | 23.2 | 1.0 | 57.2 | 3.6 | 4.4 | 33.9 | 0.9 |
| 16 | 28.6 | 0.9 | 45.8 | 3.4 | 4.3 | 45.4 | 1.1 |
| 17 | 28.3 | 1.2 | 58.5 | 5.9 | 3.9 | 30.8 | 0.9 |
| 18 | 28.7 | 1.1 | 54.9 | 5.7 | 4.0 | 34.5 | 0.9 |
| 19 | 29.2 | 1.2 | 58.2 | 4.5 | 2.9 | 33.5 | 0.9 |
| 20 | 28.1 | 1.5 | 70.5 | 8.9 | 2.8 | 17.1 | 0.6 |
| 21 | 28.1 | 1.5 | 71.8 | 7.8 | 3.1 | 16.7 | 0.6 |
| 22 | 28.6 | 1.4 | 68.9 | 6.9 | 2.9 | 20.7 | 0.6 |
| 23 | 30.8 | 1.2 | 73.8 | 5.1 | 3.4 | 17.2 | 0.6 |
| 24 | 58.1 | 0.5 | 16.2 | 1.1 | 3.5 | 77.7 | 1.6 |

*Table 1* (contd.)
*Summary of Data Obtained in Example 1*

| *Week* | *COD* | | *% Reduction* | *Remarks* |
|---|---|---|---|---|
| | *In* | *Out* | | |
| 13 | - | - | - | |
| 14 | 530 | - | - | |
| 15 | - | - | - | h |
| 16 | 275 | 115 | 58 | i |
| 17 | 395 | 165 | 58 | |
| 18 | 550 | 320 | 42 | |
| 19 | 484 | 200 | 59 | j |
| 20 | 870 | 295 | 66 | |
| 21 | 960 | 295 | 69 | |
| 22 | 470 | 175 | 63 | |
| 23 | - | - | - | k |
| 24 | 78 | 78 | 0 | |

*Table 1* continued)
*Summary of Data Obtained In Example 1*

| *Week* | *Feed Rate, ml/hr.* | *Gas Evolved ml/hr.* | *Gas Composition (mole-%)* | | | | |
|---|---|---|---|---|---|---|---|
| | | | *$CH_4$* | *$CO_2$* | *$O_2$* | *$N_2$* | *A* |
| 25 | 27.0 | 0.7 | 47.4 | 2.9 | 2.7 | 46.1 | 1.0 |
| 26 | 26.7 | 1.4 | 64.8 | 14.5 | 0.7 | 19.5 | 0.6 |
| 27 | 26.1 | 1.6 | 60.8 | 18.7 | 3.2 | 16.8 | 0.5 |
| 28 | 26.1 | 2.5 | 68.8 | 21.8 | 1.9 | 7.3 | 0.3 |
| 29 | 25.3 | 2.0 | 69.1 | 16.0 | 2.6 | 11.9 | 0.4 |
| 30 | 23.9 | 2.3 | 69.4 | 21.2 | 1.9 | 7.3 | 0.3 |
| 31 | 23.8 | 2.0 | 74.5 | 15.5 | 1.9 | 7.8 | 0.3 |
| 32 | 20.1 | 2.1 | 69.1 | 19.2 | 2.5 | 8.9 | 0.3 |
| 33 | 21.4 | 1.8 | 71.9 | 18.2 | 2.2 | 7.5 | 0.3 |
| 34 | 23.4 | 1.4 | 75.5 | 11.4 | 2.3 | 10.4 | 0.4 |

*Table 1* (contd.)
*Summary of Data Obtained In Example 1*

| *Week* | *COD* | | | |
|---|---|---|---|---|
| | *In* | *Out* | *% Reduction* | *Remarks* |
| 25 | 355 | 150 | 58 | 1 |
| 26 | 690 | 185 | 73 | m |
| 27 | 560 | 190 | 66 | |
| 28 | 1300 | 360 | 72 | |
| 29 | 680 | 155 | 77 | |
| 30 | 790 | 190 | 76 | |
| 31 | 550 | 180 | 67 | |
| 32 | 1610 | 335 | 79 | |
| 33 | 1147 | 307 | 73 | |
| 34 | - | - | - | |

*Table 1 (Continued)*

a The anaerobic reactor developed a leak in the water jacket gaskets which were then replaced.
b The peristaltic gas pump was adjusted and another leak was stopped.
c The feed pump broke down and was replaced with a Milton Roy Mini-Pump.
d The Milton Roy feed pump was replaced with an original-type Fluid Metering Pump.
e The process was allowed to run continuously, but without monitoring, for the next 17 days.
f The peristaltic gas pump was replaced with a bellows pump. Because of leaks in the bellows pump, the peristaltic gas pump was re-installed two days later. Air was bubbled into the feed for the next week.
g The passage of air into the feed was stopped.
h Water at 31°C was circulated through the aerobic reactor water jacket.
i The temperature of the aerobic reactor was increased to 34°C.
j The aerobic reactor was returned to ambient temperature operation.
k The feed was changed to primary-treated sewage.
l The feed was changed from primary-treated sewage back to raw sewage.
m A leaking tube in the gas pump was replaced.

*Example 2*

The procedure of Example 1 was repeated, except that the aerobic reactor was charged with 19 g of CGZ carrier, the carrier in the aerobic reactor was not seeded, the inorganic membrane of the anaerobic reactor was an alumina membrane and the anaerobic reactor was charged with 18.4 g of the CGZ carrier.

The alumina membrane was prepared in accordance with well-known procedures. Briefly, 300 g of SA alumina containing 3 percent, by weight, of carbowax was isostatically pressed at 1,758 kg/cm$^2$ (25,000 psi) in a mould which consisted of a cylindrical mandrel having a diameter of 1.9 cm and a cylinder with rubber sleeve having an inner diameter of 3.65 cm. The resulting cylindrical tube had the following cross-sectional dimensions: i.d., 1.9 cm; o.d. 2.62 cm. The tube was turned on a lathe to an o.d. of 2.4 cm. The tube was about 36 cm in length. The tube then was fired in a furnace as follows: The furnace was heated to 500°C (from ambient temperature) at 50°C per hour and maintained at 500°C for two hours. The temperature then was increased to 1550°C at a first rate of 50°C per hour to 950°C and a second rate of 100°C per hour to 1550°C, at which temperature the furnace was held for five hours. The furnace then was cooled at 100°C per hour to 950°C and at 50°C per hour to ambient temperature. The resulting alumina controlled-pore membrane had an i.d. of 1.43 cm, an o.d. of 1.75 cm and a wall thickness of 2.0 mm. Pore diameter distribution was from 3500 to 4500Å, with an average pore diameter of 4000Å. Wall porosity was 46.8 percent and pore volume was 0.22 cc/g. The membrane was rendered hydrophobic by placing it in 500 ml of acetone containing 10 percent octadecyl-trichlorosilane and allowing it to react over night at ambient temperature. The membrane then was removed from the acetone solution and washed four times with 50 ml portions of acetone. The membrane was air-dried for four hours and then was heated at 120°C for 1.5 hours.

The data obtained from this Example are summarized in Table II below, again as weekly averages.

*Table II*
*Summary of Data in Example 2*

| *Week* | *Feed Rate ml/hr.* | *Gas Evolved, ml/hr,* | *Gas Composition (mole-%)* $CH_4$ | $CO_2$ | $O_2$ | $N_2$ | *A* |
|---|---|---|---|---|---|---|---|
| 1 | 25.4 | 0 | - | - | - | - | - |
| 2 | 20.9 | 2.3 | 2.1 | 1.8 | 9.0 | 86.0 | 1.2 |
| 3 | 25.5 | 57 | 3.8 | 3.1 | 7.4 | 84.6 | 1.1 |
| 4 | 21.8 | 2.0 | 32.8 | 2.7 | 5.0 | 58.7 | 0.9 |
| 5 | 20.4 | 1.5 | 57.9 | 3.3 | 3.2 | 35.1 | 0.6 |
| 6 | 21.0 | 2.0 | 43.4 | 3.2 | 2.5 | 50.2 | 0.7 |

*Table II* (contd.)
*Summary of Data in Example 2*

| *Week* | *COD* *In* | *Out* | *% Reduction* | *Remarks* |
|---|---|---|---|---|
| 1 | 720 | 600 | 17 | a |
| 2 | 870 | 330 | 62 | |
| 3 | 520 | 370 | 29 | b |
| 4 | 1550 | 1000 | 35 | c |
| 5 | 1177 | 710 | 40 | |
| 6 | - | - | - | |

a Data for one day only.

b Gas leak occured; attempted to seal gas leak with tape.

c Attempted to seal gas le

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*Example 3*

The procedure of Example 1 was repeated with some changes in equipment. The aerobic reactor consisted of a Lab-Crest column, without jacket, 400 x 15 mm. The reactor was charged with 50 g of CGZ carrier. The anaerobic reactor consisted of an outer jacket 31.1 cm in length and a fritted glass membrane 30.5 cm in length and 1.6 cm in diameter. The membrane, which was fused to the outer jacket, consisted of three sections of fritted glass tubing of equal length which had been fused together. The total length of the anaerobic reactor was 40.6 cm. The membrane had a pore diameter distribution of from 3 to 6 μ and an average pore diameter of 4.5 μ. The membrane was made hydrophobic by allowing it to react with 130 ml of 10 percent octadecyltrichlorosilane in acetone at ambient temperature for about three days. The membrane then was removed from the acetone solution as washed successively with two 130 ml portions of acetone, two 130 ml portions of methanol and one 130 ml portion of acetone. The membrane was air-dried by aspiration. The anaerobic reactor was charged with 23 g of CGZ carrier. The gas pump was a Cole-Parmer Masterflex peristaltic pump.

The results are summarized in Table III below. The membrane, however, passed liquid water during the time the process was in operation, demonstrating that the pore diameters of the fritted glass membrane in general were too large.

*Table III*
*Summary of Data Obtained in Example 3*

| *Week* | *Feed Rate ml/hr.* | *Gas Evolved, ml/hr.* | *Gas Composition (mole-%)* | | | | |
|---|---|---|---|---|---|---|---|
| | | | *$CH_4$* | *$CO_2$* | *$O_2$* | *$N_2$* | *A* |
| 1 | 28.8 | 25.9 | - | - | - | - | - |
| 2 | 20.4 | 0.5 | 0.4 | 2.2 | 0.1 | 94.9 | 2.5 |
| 3 | 34.9 | 0.6 | 10.4 | 4.3 | 0 | 83.3 | 2.0 |
| 4 | 30.2 | 0.5 | 21.4 | 1.6 | 0.5 | 74.7 | 1.8 |
| 5 | 29.4 | 0.6 | 31.1 | 1.8 | 0 | 65.6 | 1.6 |
| 6 | 31.0 | 0.7 | 38.4 | 3.1 | 0.4 | 56.7 | 1.4 |
| 7 | 31.8 | 0.8 | 45.8 | 4.1 | 0.1 | 48.9 | 1.2 |
| 8 | 32.4 | 1.2 | 53.2 | 5.2 | 0 | 40.5 | 1.0 |
| 9 | 34.0 | 1.6 | 66.9 | 7.6 | 0.3 | 24.6 | 0.7 |
| 10 | 34.0 | 1.6 | 67.4 | 8.0 | 0.3 | 23.7 | 0.7 |
| 11 | 33.9 | 0.9 | 69.2 | 5.3 | 0.4 | 24.4 | 0.7 |
| 12 | 35.0 | 0.3 | 72.5 | 4.7 | 0.2 | 22.0 | 0.6 |

*Table III* (contd.)
*Summary of Data in Example 3*

| Week | COD | | | Remarks |
|---|---|---|---|---|
| | In | Out | % Reduction | |
| 1 | - | - | - | a |
| 2 | - | - | - | b |
| 3 | - | - | - | c |
| 4 | - | - | - | |
| 5 | 270 | 190 | 30 | |
| 6 | 325 | 225 | 31 | |
| 7 | - | - | - | |
| 8 | 350 | 198 | 43 | |
| 9 | 650 | 328 | 50 | |
| 10 | 765 | 342 | 55 | |
| 11 | 445 | 220 | 51 | |
| 12 | - | - | - | |

a Leak in anaerobic reactor; attempted to seal the leak with appropriate clamps.

b Adjusted anaerobic reactor to a horizontal position and made certain that reactor was irradiated by sunlight and over-head lights.

c A red microbial growth was obseved on the exterior surface of the membrane.

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CLAIMS

1. A controlled-pore, hydrophobic inorganic membrane wherein at least 90 percent of the pores have diameters of from 100 to 10,000Å.

2. A membrane as claimed in claim 1 wherein the pore diameter is from 900 to 9,000Å.

3. A membrane as claimed in claim 2 wherein the pore diameter is from 1,500 to 6,000Å.

4. A membrane as claimed in any of claims 1 to 3 wherein the membrane is composed of a siliceous material.

5. A membrane as claimed in claim 4 wherein the siliceous material is glass.

6. A membrane as claimed in claim 4 wherein the siliceous material is silica.

7. A membrane as claimed in any of claims 1 to 3 wherein the membrane is composed of a non-siliceous material.

8. A membrane as claimed in claim 7 wherein the non-siliceous material is alumina.

9. A membrane as claimed in any of claims 1 to 8 which is rendered hydrophobic by a post-formation treatment.

10. A membrane as claimed in claim 9 which is rendered hydrophobic by treatment with octadecyltrichlorosilane.

11. A membrane as claimed in claim 1 substantially as herein described.

12. A membrane as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

13. A process for the production of a membrane as claimed in claim 1 substantially as herein described.

14. A membrane when produced by a process as claimed in claim 13.

15. A process for preferentially extracting one or more hydrophobic gases from a mixture of hydrophobic and hydrophilic gases which comprises:
(a) presenting such a mixture membrane as claimed in claim 1; and
(b) withdrawing from the other side of the membrane a hydrophobic gas-enriched mixture of gases.

16. A process as claimed in claim 15 in which the gas mixture is present in conjunction with an aqueous medium.

17. A process as claimed in claim 16 in which the hydrophobic and hydrophilic gases are methane and carbon dioxide, respectively.

18. A process as claimed in claim 15 substantially as herein described.

19. A process as claimed in claim 15 substantially as herein described with reference to any one of the Examples.

20. A hydrophobic gas-enriched mixture of gases resulting from a process as claimed in any of claims 15 to 19.

21. The invention substantially as herein described.

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